INTEGRATION OF NITRIFICATION WITH DENITRIFICATION FOR WATER TREATMENT

Luong Van Anh[1], Nguyen Thuy Linh[1], Duc Toan Do[2]

Abstract: *With poor water catchment protection, surface water and groundwater sources can be polluted by many substances, of which, ammonia is one of the primary factors. While conventional methods for ammonia treatment using chlorine present limitations during treatment processes, biological treatment solutions are highly appropriate in efficiently removing contaminants such as ammonia. The study was conducted by an experiment at the lab-scale focused on the integration of a nitrification system with a denitrification system to remove ammonia and other nitrogen compounds in treatment surface water and groundwater. The results revealed that the nitrification system with hydraulic rate of 0.3 L min^{-1} can remove 83 mg NH_4-N day^{-1} with 4.88 m^2 of polypropylene media. It corresponds to 17 mg NH_4-N m^{-2} day^{-1} of ammonium nitrogen surface load. Meanwhile, 716 mg NO_3-N day^{-1} was eliminated by the denitrification system with hydraulic rate of 42 ml min^{-1}.*

Keywords: Nitrogen, ammonia, nitrification, denitrification, barley straw.

1. INTRODUCTION

With the expanse of major cities led by the population boom over the world and poor water catchment protection, water sources including both surface water and groundwater have been affected by a deterioration of both quantity and quality. Human activities in catchment areas are believed to be a main reason for these issues (Henry & Heineke 1996). Surface water and groundwater sources can be polluted by many substances, of which ammonia is one of the primary factors. The ammonia content in these water sources varies from over 0 mg NH_4^+ L^{-1} to 25 mg NH_4^+ L^{-1} (Angelopoulos et al. 2009). The low concentration of ammonium nitrogen (under 5 mg NH_4^+ L^{-1}) has been recorded in a number of sources. Ammonia seriously influences chlorine disinfection processes which is an important stage in drinking water treatment (van den Akker 2008). Therefore, the ammonia contamination should be considered in order to minimize its negative effects.

In the context of the water quality deterioration by nitrogen in recent decades, the demand for ammonia removal in potable water treatment plants is increasing. Meanwhile, conventional methods for ammonia treatment using chlorine present limitations during treatment processes. This conventional approach uses pre-chlorination as an effective solution to eliminate ammonia in raw water. However, this approach has a number of disadvantages such as generating disinfection by-products and increasing chlorine consumption (van Den Akker et al. 2010). By-products such as chloramine will lead to poor treated water quality and can cause public health problems. Furthermore, in order to eliminate 1mg ammonia, an amount of chlorine 10 mg is required which could significantly increase the water treatment cost. Therefore, it is necessary to develop environment friendly approaches for ammonia removal.

Biological treatment solutions are highly appropriate in efficiently removing contaminants such as ammonia because they can minimize chlorine consumption and disinfection by-products generated by the interference between ammonia and chlorine during the disinfection

[1] *National Centre for Rural Water Supply and Environmental Sanitation.*
[2] *CETA Architecture and Construction Technology Consultancy JSC.*

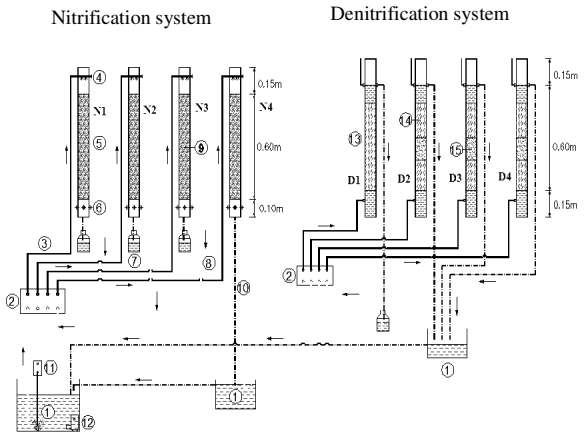
process. Hence, biological methods to remove nitrogen in water sources have been studied since the early 1990s (Pearce & Williams 1999). While nitrification is known as one effective option to biologically convert ammonia into nitrate, which does not increase chlorine demand for disinfection, denitrification is indicated as a powerful solution to transfer nitrate into nitrogen gas which is released into the atmosphere. Unfortunately, most of this research has focused on either nitrification or denitrification processes. Meanwhile, only a few researchers have investigated combining nitrification with denitrification models such as Completely Autotrophic Nitrogen removal over Nitrite (CANON), Aerobic Deammonification (DEMON), Oxygen-Limited Autotrophic Nitrification Denitrification (OLAND), and Simultaneous Partial Nitrification, Anammox and Denitrification (SNAD). Nevertheless, these studies were regularly conducted on wastewaters, which have extremely high nitrogen concentrations compared with those in surface water and groundwater. Hence, further study on the integration of nitrification with denitrification is necessary at lower concentrations of ammonia contamination.

2. METHODS

2.1. Preparation

The pilot system including nitrification and denitrification systems was designed as given in Figure 1. The nitrifying trickling filters (NTFs) were packed in four polyvinyl chloride columns (0.104 m internal diameter, height 0.85 m). The filters used a bed (thickness, 0.6 m and volume 0.0051 m^3) of TKP 312 (2H Plastic Australia) polypropylene with area to volume ratio of 240 m^2 m^{-3}, void volume of 95% and average foils thickness of 0.35 mm. The effective filter surface area (1.22 m^2) of each filter was similar. The 4 NTFs were operated in series, with water distribution on to the top of the NTFs by a peristaltic pump at a constant flow rate of 0.3 L min^{-1}. The system operated under recirculated flow. The nitrification process naturally occur by specialized bacteria such as *Nitrosomonas sp.* and *Nitrobacter sp.*

In comparison with the biological nitrification process, types of bacteria in the biological denitrification process are diversified and they prefer to organic carbon for their activations. Denitrification system was divided into three groups: Group 1 comprised the first two columns in the series, Group 2 was the third column and Group 3 with the last column. The inside diameter of each column is 0.104 m and 0.9m in height. Barley straw (200g/filter) provided organic carbon for the denitrifying processes, while spongy iron was included to assist in elimination of dissolved oxygen in the water. Barley straw (1.0–3.0 mm in diameter) was collected from a farm after a crop in South Australia, while spongy iron (60.60 % of Fe0; 0.425–1.000 mm in diameter) was obtained from Kaibiyuan Co., Beijing, China.



1- Plastic reservoir, 2- Peristaltic pump, 3- Discharge silicone tube, 4- Spray distribution, 5- Nitrifying column, 6- Natural ventilation ports, 7- Glass reservoir, 8- Intake silicone tube, 9- Polypropylene media, 10- Returned silicone tube, 11- Air pump, 12- Stirring pump, 13- Denitrifying column, 14- Barley straw, 15- Spongy iron

Figure 1. The schematic diagram of nitrification and denitrification systems

2.2. Methods

In the study, the experiment was divided into four main phases including Commissioning phase, Experimental phase 1, Experimental phase 2 and Experimental phase 3. In the commissioning phase, nitrifying bacteria were

developed in NTFs in the presence of ammonium spiked lake water. After that, all water in the system was replaced by new lake water spiked with ammonium in the Experimental phase 1. This Phase assisted to basically define the capacity of nitrification and denitrification systems. Thereafter, maximum capacity of the nitrification and denitrification systems were measured in the Experimental phase 2 and 3 respectively.

2.3. Sampling and data analysis

During the experiment, lake water that was prepared for the experiment was sampled. Additionally, influent and effluent samples of each column of both nitrification and denitrification systems was collected daily. About 50 ml of water was collected for each sample at 11am (± 1h). At the same time of sampling, the dissolved oxygen (DO), the temperature and the potential of hydrogen (pH) was measured by a DO meter and a pH meter. The samples were filtered through glass microfiber filters (exclusion size, 4 µm) before analysis. This filtration can assist to eliminate negative effects of sediment on the analysis results of ammonium, nitrite and nitrate concentrations.

All lake water samples were measured free and total chlorine by HACH DR 2000. These measurements are necessary because chlorine in lake water can interact with ammonium to reduce the concentration of ammonium in water samples. Water samples were analysed for total organic carbon (TOC), inorganic carbon (IC) were analysed by TOC-L Shimadzu Analyzer. Ammonium (NH_4-N), nitrite (NO_2-N) and nitrate (NO_3-N) were analysed as described in Standard Methods for the Examination of Water and Wastewater (Greenberg et al., 1992) using a FOSS - FIAstar 5000 Analyzer.

3. RESULTS

The Commissioning phase was conducted over 20 days. In the first 14 days, the effectiveness of the system was limited. The concentration of nitrate and nitrite was constant and under 0.15 mg L^{-1}. However, the nitrate mass formed significantly increased to 1.0 mg L^{-1} in the following day, while this mass of nitrite also reached to over 0.3 mg L^{-1}. After that the nitrate production remained constant, reducing after day 7. Furthermore, the change in ammonium, nitrate and nitrite also were measured at influent and effluent points of all denitrification columns. The ammonium concentrations in denitrifying columns were quite high in the first days. They were between over 1.0 and 5.5 mg NH_4-N L^{-1}. While the influent ammonium concentration was only below 0.5 mg NH_4-N L^{-1}.

The Experimental phase 1 includes two stages and was conducted over 14 days to determine the efficiency of both nitrification and denitrification systems. The initial concentration of ammonium in the nitrification system was 4.3 mg NH_4-N L^{-1}. This concentration reduced to 1.9 mg NH_4-N L^{-1} after 24 hours and 0.034 mg NH_4-N L^{-1} after 48 hours. Then ammonium was not detected in the nitrifying reservoir and effluent point of the system during following days of the Phase. The average daily rate of nitrification achieved to be over 2.1 mg NH_4-N L^{-1} (75 mg NH_4-N day^{-1}). Meanwhile, no nitrate and nitrite were detected at effluent flows of Columns 2, 3 and 4, a small concentration of nitrate < 0.1 mg NO_3-N L^{-1} was detected in Column 1.

Experimental Phase 2 was conducted during 13 days. While only very low nitrite concentrations under 0.06 mg NO_2-N L^{-1} were found at both influent and effluent points, nitrate concentrations were quite high. In the first day of the Phase, over 8.4 mg NO_3-N L^{-1} was detected in the system and it reached a peak at around 9.5 mg NO_3-N L^{-1} in the following day. However, nitrate concentration in the nitrification system began declining from day 3 to day 6 before stabilising around 6.2 mg NO_3-N L^{-1} during the rest of Phase 2.

The last experimental phase was conducted over five days. Initial nitrate concentration in denitrifying columns were 22.86 mg NO_3-N L^{-1}.

After 24 hours, nitrate concentration in the reservoir remained over 7 NO_3-N L^{-1}, while these figures in Column 3 and 4 were 2.3 NO_3-N L^{-1} and 0.36 NO_3-N L^{-1} respectively. In Column 1 and 2 of Group 1, nitrate was not detected at the effluent discharge points.

4. DISCUSSION

4.1. Nitrification performances

The performances of the nitrification system was evaluated in two steps. In the first step, the nitrification was primarily defined as its capacity to converting ammonium to nitrate and nitrite. This step was conducted in the first stage of Experimental Phase 1. Based on this primary calculation, the average maximum capacity of the nitrification system was determined in the next step which was presented as Experimental Phase 2.

In order to basically define nitrifying capacity, 150 mg NH_4-N was added to 35 L of water in the nitrifying reservoir. The initial ammonium concentration was 4.3 mg NH_4-N L^{-1}. The results indicated that after one day, ammonium concentration in the reservoir significantly reduced to 1.9 mg NH_4-N L^{-1}. In the next day, this value was 0.034 mg NH_4-N L^{-1} and no ammonium was found in the following days. These ammonium concentrations were not original values because water in the nitrifying reservoir was diluted by return flows 4.2 ml min^{-1} (6.05 L day^{-1}) from the denitrification system. The original ammonium concentration values at the nitrifying reservoir were 2.3 mg NH_4-N L^{-1} and 0.04 mg NH_4-N L^{-1} for the first and second day respectively. They were defined as Equation 4.1 below (Doucette 1997).

$$C_1 = \frac{C_2 x V_2}{V_1} \qquad \text{(Eq. 4.1)}$$

$$V_1 = V - V_d \qquad \text{(Eq. 4.2)}$$

Where C_1 is original ammonium concentration at the measure time (mg NH_4-N L^{-1}); C_2 is diluted ammonium concentration at the measure time (mg NH_4-N L^{-1}); V_1 is original water volume in the nitrifying reservoir (V_1 = 28.95 L) and is defined as Equation 4.2; V_2 is diluted volume of water in the nitrifying reservoir (V_2 = 35 L); V is initial volume of water in the nitrifying reservoir (V = V_2 = 35L); V_d is volume of water pumped to the denitrification per day V_d = 6.05 L.

The converted rate of ammonium in the first day was 2.0 mg NH_4-N L^{-1} and this figure was 2.26 mg NH_4-N L^{-1} in the second day. Basically, the average converted rate of ammonium in the nitrification system was 2.13 mg NH_4-N L^{-1} day^{-1}. It was equal to a mass of 75 mg NH_4-N converted per day by the system as a whole. The data analysis of ammonium showed that no ammonium was detected in denitrification columns during the stage.

The data in Figure 2 indicated that most of ammonium mass was converted to nitrate and nitrite in the first two days. In the first day, 1.36 mg NO_3-N L^{-1} was formed in comparison with 0.2 mg NO_2-N L^{-1}. The remaining ammonium concentration was 1.9 mg NH_4-N L^{-1}. The total values of ammonium, nitrate and nitrite concentration was 3.46 mg L^{-1}. This concentration was diluted by return flow from the denitrification system, therefore it is necessary to convert to original value by Equation 4.1 and 4.2. As a result the total original concentration of ammonium, nitrate and nitrite was 4.18 mg L^{-1} compared to 4.3 mg L^{-1} in the influent. It is obvious to recognize that 2.8% (0.12 mg L^{-1}) of influent mass was unaccounted for after one day. The deficient mass could be explained by a small amount of nitrate and nitrite were pumped to the denitrification system and were converted to nitrogen gas. Similarly, the decline of total ammonium, nitrate and nitrite in following days can also be explained in the same way.

However, in day 2, the original total values of ammonium, nitrate and nitrite concentration was nearly 4.45 mg L^{-1} (diluted concentration value was 3.68 mg L^{-1}). This number was 3.5% higher than the initial value 4.3 mg L^{-1}. In reality, it is not simple to obtain 100% mass balance in complex experimental systems, various factors could affect experimental results.

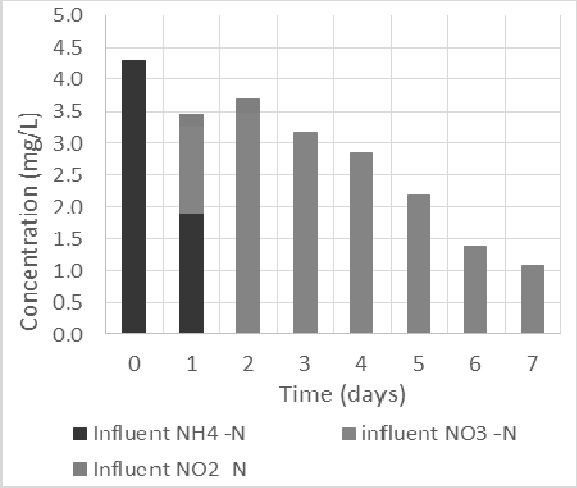


Figure 2. Ammonium, nitrate and nitrite in the nitrifying reservoir during the first stage of Experimental Phase 1

Based on the primary capacity of the nitrification system, the next step was conducted as Experimental Phase 2. The selected ammonium mass was 150 mg NH_4-N day^{-1} which was twice that compared to the initial value of 75 mg NH_4-N day^{-1}. It was selected because the loss of ammonium mass could be higher when a part of the ammonium was pumped to denitrifying columns.

The converted ammonium masses were calculated based on Equation 4.3 below. The results indicated that in the first two days, converted ammonium masses were unusual. While 144 mg NH_4-N was converted in the first day, this figure was only 20mg NH_4-N in the second day. In the following days converted ammonium masses fluctuated around the average value which was nearly 83 mg NH_4-N per day.

$$M_c = M_{in} - M_{out} \quad \text{(Eq. 4.3)}$$

$$M_{out} = \sum C_i.V_i \quad \text{(Eq. 4.4)}$$

Where M_c is daily mass of ammonium was converted (mg); M_{in} is total daily input ammonium mass (mg); M_{out} is total daily output ammonium mass (mg) and M_{out} is measured as Equation 3.7; C_i and V_i are daily ammonium concentrations and volumes of each nitrifying and denitrifying columns.

Figure 3 shows the total converted ammonium mass during 13 days of the Experimental Phase 2. During this phase, 1650 mg NH_4-N was added to the system, of which nearly 1077 mg NH_4-N was converted to nitrate and nitrite, with only 573 mg NH_4-N remaining. The average ammonium removal rate was 83 mg NH_4-N day^{-1}. It corresponds to 0.2 mg NH_4-N L^{-1} h^{-1}. Although this rate was higher than that in the Experimental Phase 1, it was not considered overly high. In a study, Mai et al. (2016) achieved ammonia removal rate of 0.44 mg NH_4-N L^{-1} h^{-1}. The pilot in their study was quite similar to the nitrification system in this study, however, installation of nitrifying columns was parallel rather than in series as in this study. The ammonium conversion rate in the study could not achieve a higher level because the external energy source for nitrifying bacteria was limited.

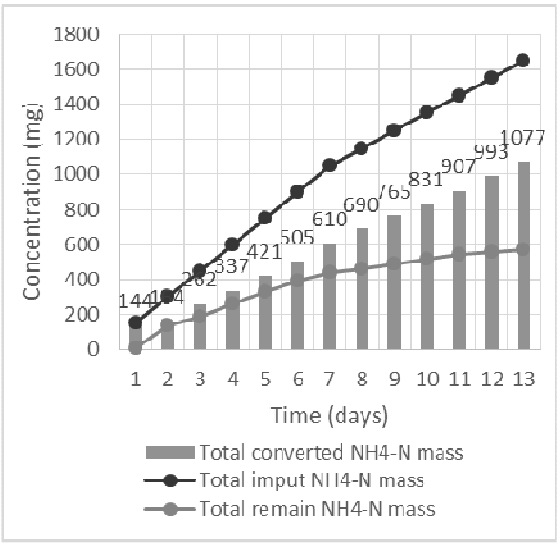


Figure 3. Defining total converted ammonium mass 1

4.2. Denitrification performances

The primary average capacity of the denitrification system was defined to be approximately 0.62 mg NO_3-N L^{-1} day^{-1} in the Experimental Phase 1. The result was calculated based on the second stage of the Experimental Phase 1. As shown in Figure 4, initial total ammonia nitrogen including ammonium, nitrate

and nitrite during this period fluctuated around 70 mg day^{-1}. After a day, this number significantly reduced to around 40 mg day^{-1}. This reduction was caused by the removal of nitrate from the denitrification system. This system removed daily over 30 mg NO_3-N. The nitrate removal rate was only a primary value because it was calculated based on the denitrification flow rate 4.2 ml min^{-1}. The rate could change if nitrate concentration or flow rate was not stable (Wang et al. 2013). This theory is in line with previous studies. For example, Park, Choi and Pak (2005) conducted a denitrification study with an initial nitrate concentration in the range of 20 mg NO_3-N L^{-1} to 150 mg NO_3-N L^{-1}. Their results revealed that the nitrate removal rate depended on initial nitrate concentration. The removal rate increased when nitrate loading increased. Similarly, the change in nitrate removal rate was observed in a study by Park et al. (2005) where the initial nitrate concentration changed from 20 mg NO_3-N L^{-1} to over 490 mg NO_3-N L^{-1}.

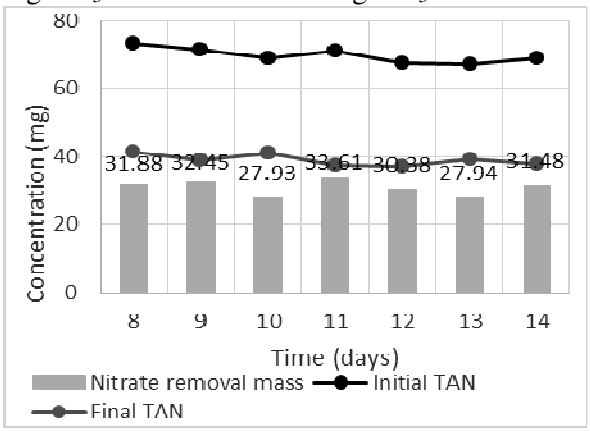


Figure 4. Total ammonia nitrogen (TAN) and nitrate removal mass in Phase 1

Although influent nitrate concentration at the end of Phase 2 was quite high an approximately 6.0 mg NO_3-N L^{-1}, in an attempt to achieve nitrate at effluent points, indicative of the maximum denitrification rate, of denitrifying columns, denitrification flow rates increased three times from 1.5, 1.2 and 1.5 ml min^{-1} to 4.5, 3.6 and 4.5 ml min^{-1} for group 1, 2 and 3 respectively. However after four days of the Experimental Phase 3, no nitrate or nitrite were detected at effluent points of the denitrifying columns. This result demonstrated that the capacity of the denitrification was much higher, and the finding is in agreement with previous studies which revealed that the efficiency of denitrification systems was high. These studies found that large amount of nitrate (approximately 13 mg L^{-1}) could be converted to nitrogen gas in a short time (Schmidt & Clark 2012).

Figure 5 below presents trends in concentration of influent ammonium and nitrate at the nitrifying reservoir. It is clear that while ammonium concentration had an increasing trend during the time, nitrate concentration which was produced from influent ammonium was on a continual decline. Ammonium concentration increased from over 10 mg NH_4-N L^{-1} to nearly 15 mg NH_4-N L^{-1} in four days. Conversely, nitrate concentration decreased by approximately 1.6 mg NO_3-N L^{-1} from 3.2 mg NO_3-N L^{-1} to 1.6 mg NO_3-N L^{-1}. From the data, it could be inferred that the ammonium removal rate reached maximum capacity and, therefore, could not produce more nitrate. Meanwhile, nitrate mass could disappear in next several days. Therefore, a decision was made to stop the system and change the method for defining the maximum capacity of the denitrification system.

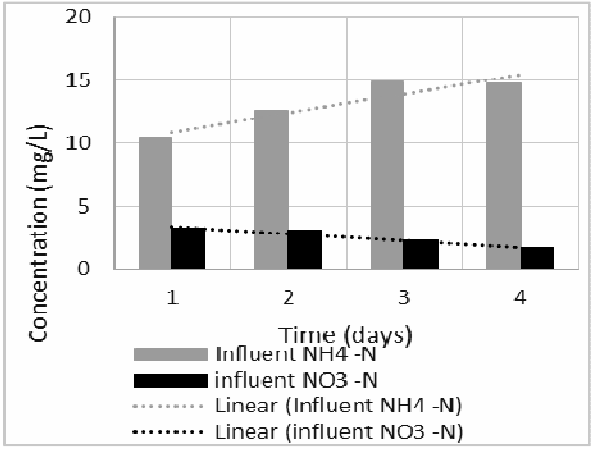


Figure 5. Ammonium and nitrate in the nitrifying reservoir

Accordingly, the nitrification system which was applied to provide nitrate to the denitrification system by converting ammonium

to nitrate was stopped. An external nitrate source was utilized as influent nitrate to the denitrifying columns. In addition, the denitrification flow rates were increased 10 times and the sampling time was changed from daily to hourly. All changes were made to ensure that nitrate could be found at effluent points of the denitrification system and, as a result, effluent nitrate was detected from the denitrification columns, indicating saturation of the denitrification capacity of the columns.

Total nitrate removal mass was calculated based on Equation 4.3 and 4.4 in which ammonium mass was replaced by nitrate mass. The results are shown in Figure 6 below. Input nitrate mass was 800 mg NO_3-N, and after 24 hours this mass remained 84 mg NO_3-N. Consequently, 716 mg NO_3-N was converted to nitrogen gas in a day at a total flow rate was 42 ml min^{-1}. It equates to a nitrate removal rate of approximately 11 mg NO_3-N L^{-1} h^{-1}. The efficiency of the denitrification system was contributed to by the capacity of three Groups of denitrifying columns. Group 1 with denitrifying column 1 and 2 accounted for over 43%of the total nitrate removal mass. Group 2 and 3 contributed nearly 22 and 35% respectively. The efficiency of Group 1 was highest because it combined two denitrifying columns while Group 2 and 3 only had one column.

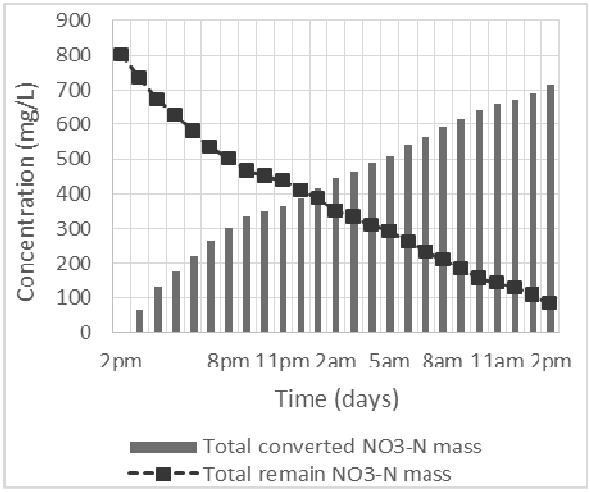


Figure 6. Total converted and remaining nitrate in a day of the denitrification system in Experimental Phase 3

5. CONCLUSION

In conclusion, this study indicated that the nitrification system can remove 83 mg NH_4-N day^{-1} with 4.88 m^2 of polypropylene media. This corresponds to 17 mg NH_4-N m^{-2} day^{-1} of ammonium nitrogen removal per unit surface area of the filter. While, 716 mg NO_3-N was eliminated by the denitrification system, Column 1 and 2 accounted for over 43% of the total nitrate nitrogen removal mass. These figures were nearly 22% and 35% contributed to by Column 3 and 4 respectively.

REFERENCES

Angelopoulos, K, Spiliopoulos, I, Mandoulaki, A, Theodorakopoulou, A & Kouvelas, A 2009, "*Groundwater nitrate pollution in northern part of Achaia Prefecture*", Desalination, vol. 248, no. 1, pp. 852-8.

Doucette, LJ 1997, *Mathematics for the Clinical Laboratory*, W.B. Saunders Company.

Henry, JG & Heineke, GW 1996, "*Environmental science and engineering*", Environment International, vol. 6, no. 22, p. 764.

Mai, L, van den Akker, B, Du, J, Kookana, RS & Fallowfield, H 2016, "*Impact of exogenous organic carbon on the removal of chemicals of concern in the high rate nitrifying trickling filters*", Journal of Environmental Management, vol. 174, pp. 7-13.

Park, HI, Choi, Y-J & Pak, D 2005, "*Autohydrogenotrophic denitrifying microbial community in a glass beads biofilm reactor*", Biotechnology letters, vol. 27, no. 13, pp. 949-53.

Park, HI, kun Kim, D, Choi, Y-J & Pak, D 2005, "*Nitrate reduction using an electrode as direct electron donor in a biofilm-electrode reactor*", Process Biochemistry, vol. 40, no. 10, pp. 3383-8.

Pearce, P & Williams, S 1999, "*A Nitrification Model for Mineral-Media Trickling Filters*", Water and Environment Journal, vol. 13, no. 2, pp. 84-92.

Schmidt, CA & Clark, MW 2012, "*Efficacy of a denitrification wall to treat continuously high nitrate loads*", Ecological Engineering, vol. 42, pp. 203-11.

van den Akker, B 2008, *Removal of ammonia from drinking water by biological nitrification in a fixed film reactor*, Flinders University, School of Medicine.

Van den Akker, B, Holmes, M, Cromar, N & Fallowfield, H 2010, "*The impact of organic carbon on the performance of a high rate nitrifying trickling filter designed to pre-treat potable water*", Water Science & Technology, vol. 61, no. 7.

Wang, R, Feng, Q, Liao, T, Zheng, X, Butterbach-Bahl, K, Zhang, W & Jin, C 2013, "*Effects of nitrate concentration on the denitrification potential of a*".

Tóm tắt:

KẾT HỢP QUÁ TRÌNH NITRÁT HÓA VÀ KHỬ NITƠ TRONG XỬ LÝ NƯỚC

Do còn nhiều hạn chế trong việc quản lý và bảo vệ các lưu vực thu nước nên hiện nay nhiều nguồn nước mặt và nước ngầm bị ảnh hưởng không nhỏ bởi các nguồn gây ô nhiễm khác nhau, trong đó amoniac là một trong những nguyên nhân chính. Trong khi các phương pháp xử lý amoniac truyền thống bộc lộ nhiều hạn chế khi sử dụng clo trong quá trình xử lý nước thì xử lý amoniac bằng phương pháp sinh học được xem như giải pháp tối ưu trong việc loại bỏ các chất gây ô nhiễm như amoniac. Nghiên cứu này được thực hiện trong phòng thí nghiệm và tập trung vào việc kết hợp quá trình nitrát hóa và quá trình khử nitơ để loại bỏ amoniac và các hợp chất của nó trong quá trình xử lý nước mặt và nước ngầm. Các kết quả nghiên cứu chỉ ra rằng, quá trình nitrát hóa với lưu lượng dòng chảy là 0.3 L/phút chảy qua đệm sinh học có diện tích 4.88 m^2 có thể giúp loại bỏ 83 mg NH_4-N/ngày. Lượng amoniac này tương đương với tải trọng bề mặt là 17 mg NH_4-N m^{-2} /ngày. Trong khi quá trình khử nitơ với lưu lượng dòng chảy là 42 ml/phút có thể giúp loại bỏ 716 mg NO_3-N/ngày.

Từ khóa: Nitơ, ammonia, nitrát hóa, khử nitơ, rơm.

Ngày nhận bài: *09/8/2017*

Ngày chấp nhận đăng: *22/8/2017*